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Stability of surface layers from a study of the mean-square displacements of surface atoms

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We consider the mean-square displacements (MSD) of atoms situated in a physisorbed monolayer. These MSD are found to diverge logarithmically when the ratio between the force constant coupling the physisorbed atoms to the substrate and the force constant coupling the physisorbed atoms between themselves is diverging. When going towards the bulk, the difference between the surface MSD and the bulk one is proportional to the inverse of the depth.

I. INTRODUCTION

A great deal of theoretical and experimental activity has been expended on the study of the effect of a surface with and without adsorbate on the lattice vibrations of a crystal.[1,2] There have been a number of works in recent years (reviewed in Refs. 1 and 2) which have calculated the atomic mean-square displacements (MSD) for a variety of surfaces and a wide range of temperatures. Other experimental and theoretical studies[3–5] of the MSD of adsorbed atoms have been made. However, to our knowledge, the stability of a monolayer of physisorbed atoms was not discussed from the point of view of the mean-square displacements. The purpose of this paper is to go into such a discussion.

It is well known that a two-dimensional solid is unstable against long-wavelength acoustic vibrations: the mean-square displacements of its atoms are infinite.[6] We will therefore study the physisorbed monolayer especially for these long-wavelength phonons.

We choose a model[7] sufficiently simple to have analytic results for the mean-square displacements. While the model is highly oversimplified, we feel it allows us to display the principal qualitative effects.[8] It has already been used[9,10] to estimate several physical properties of bulk and surface effects, and has been discussed at some length.[8]

Let us call (Fig. 1) β, β', and β'' the force constants coupling, respectively, the bulk atoms between themselves, the physisorbed atoms to the substrate atoms, and the physisorbed atoms between themselves. When β' is going to zero, the mean-square displacements of the physisorbed atoms are found to behave as $\ln(\beta''/\beta')$. This effect penetrates into the bulk as the inverse of the depth.

In Sec. II we introduce the phonon model and derive the above result in a "frozen-substrate" model.[11] In Sec. III we present the general expressions which enable us to calculate the high-temperature MSD and their damping into the bulk. In Sec. IV we give the general results.

II. "FROZEN-SUBSTRATE" CASE

In this section we first describe the very simple model[7] we have chosen to represent the phonon field of the semi-infinite crystal. Then we give the perturbation due to one adsorbed monolayer. Finally, we derive the expressions for the MSD at high temperatures and their variation as they go away from the surface.

We assume the crystal to be a monatomic simple cubic crystal with a (001) surface (see Fig. 1). The lattice vibrations are described by the model introduced by Rosenstock and Newell and popularized by Montroll and Potts.[7] Let $u_\alpha(\vec{l})$ denote the α component of the displacement from equilibrium of the atom at site $\vec{X}(l) = a_0(l_1\hat{x} + l_2\hat{y} + l_3\hat{z})$, where a_0 is the lattice parameter. The potential energy Φ associated with the lattice vibrations has the simple form

$$\Phi = \tfrac{1}{4}\beta \sum_{\vec{l}} \sum_{\vec{\delta}} \sum_{\alpha} [u_\alpha(\vec{l}) - u_\alpha(\vec{l}+\vec{\delta})]^2, \quad \alpha = x, y, z\ . \tag{1}$$

Here β is the nearest-neighbor force constant, and the sum over $\vec{\delta}$ is restricted to first neighbors of the atom $\vec{l}$. For an atom in the surface layer ($l_3 = 1$), one neighbor is missing, so the sum over $\vec{\delta}$ is confined to the five nearest neighbors in this case. In this model, the equations of motion are

$$\beta \sum_{\vec{\delta}} [u_\alpha(\vec{l}+\vec{\delta}) - u_\alpha(\vec{l})] - M\omega^2 u_\alpha(\vec{l}) = 0\ , \tag{2}$$

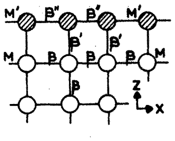

FIG. 1. Model of interaction used.

where M is the mass of the atoms. In matrix notation, Eq. (2) can be written

$$\underline{\underline{\mathrm{L}}}\,\underline{\mathrm{u}}=0\;. \tag{3}$$

We now want to modify the model (see Fig. 1) by changing to M' the mass of the surfaces atoms, and, respectively, to β' and β'' the adsorbate-substrate and adsorbate-adsorbate force constants. After taking due account of the translational symmetry in the directions $\hat{x}$ and $\hat{y}$ parallel to the surface, this perturbation to the equation of motion of the free surface crystal may be written

$$\begin{aligned}\delta L(l_3l_3')=[(M-M')\omega^2+\beta'-\beta+2(\beta''-\beta)\\ \times(2-\cos\phi_x-\cos\phi_y)]\,\delta_{l_31}\delta_{l_3'1}+(\beta-\beta')\\ \times(\delta_{l_31}\delta_{l_3'2}+\delta_{l_32}\delta_{l_3'1}-\delta_{l_32}\delta_{l_3'2})\;,\end{aligned} \tag{4}$$

where $\vec{\phi}=\vec{\mathrm{k}}a_0$ is the product of the propagation vector and of the lattice parameter.

Let us now study the case of a "frozen substrate." The adsorbed monolayer is allowed to vibrate and the substrate atoms are frozen.[11] The frequencies of vibrations of the adsorbed atoms are

$$M'\omega_\alpha^2\simeq\beta'+2\beta''(2-\cos\phi_x-\cos\phi_y)\;. \tag{5}$$

At high temperatures, the mean-square displacements of these atoms in the direction α are[1,2]

$$\langle\!\langle u_\alpha^2(1)\rangle\!\rangle\simeq k_BT\sum_{\phi_x\phi_y}\frac{1}{M'\omega_\alpha^2}\;. \tag{6}$$

The elastic limit contribution is

$$\langle\!\langle u_\alpha^2(1)\rangle\!\rangle\simeq\frac{k_BT}{2\pi}\int_0^{\phi_L}\frac{\phi\,d\phi}{\beta'+\beta''\phi^2}\;, \tag{7}$$

where

$$\phi^2=\phi_x^2+\phi_y^2\;. \tag{8}$$

Finally, for $\beta'\ll\beta''$,

$$\langle\!\langle u_\alpha^2(1)\rangle\!\rangle\simeq(k_BT/4\pi\beta'')\ln[1+(\beta''/\beta')\phi_L^2]\;, \tag{9a}$$

where ϕ_L is the limit value of ϕ for which the elastic approximation remains valid. Here we assumed the lattice to be perfect and to extend to infinity in directions parallel to the surface. But for real surfaces, the range of parallel perfection may be limited in an area of radius r_0 thereby fixing a nonzero lower limit $(2\pi a_0/r_0)$ on integral (7). Then, for $\beta'\ll\beta''$,

$$\langle\!\langle u_\alpha^2(1)\rangle\!\rangle\simeq\frac{k_BT}{4\pi\beta''}\ln\left|\frac{1+(\beta''/\beta')\phi_L^2}{1+(\beta''/\beta')(2\pi a_0/r_0)^2}\right|\;, \tag{9b}$$

where ϕ_L is of the order of unity.

The result (9b) shows that the behavior displayed in (9a) is physically significant for $r_0/a_0\gg2\pi(\beta''/\beta')^{1/2}$. Even if we take a ratio $\beta''/\beta'\simeq100$, we see that flat surfaces such that $r_0/a_0\gg100$ are easily prepared, for example with a monolayer of rare gas on graphite.[12] This shows then that these physisorbed monolayers are stabilized by the interactions with the substrate and not by the finite range of parallel perfection of the surface.

Let us now justify by an exact analysis the "frozen-substate" approximation used above.

III. FORMALISM

In general, at high temperatures, the mean-square displacements[1,2] of atom $\vec{l}$ in the direction α may be written in the form

$$\langle\!\langle u_\alpha^2(\vec{l})\rangle\!\rangle\simeq-k_BT[U_{\alpha\alpha}(\vec{l},\vec{l})]_{\omega^2=0}\;, \tag{10}$$

where

$$\underline{\underline{\mathrm{U}}}\equiv(\underline{\underline{\mathrm{L}}}+\delta\underline{\underline{\mathrm{L}}})^{-1} \tag{11}$$

is the so called Green's function for the crystal with the adsorbed layer.

The virtue of using the Montroll-Potts model is that the Green's function $\underline{\underline{\mathrm{U}}}^{(s)}$ for the crystal with a clean (001) surface, is of a rather simple form. We can write

$$\begin{aligned}U_{\alpha\beta}^{(s)}(\vec{l},\vec{l}')=\frac{1}{N_s}\sum_{\phi_x\phi_y}U_{\alpha\beta}^{(s)}(\phi_x\phi_y,\,l_3l_3')\\ \times e^{i\phi_x(l_1-l_1')}e^{i\phi_y(l_2-l_2')}\,,\end{aligned} \tag{12}$$

where N_s is the number of atoms in a (001) plane. Then for the Montroll-Potts model studied here,[13]

$$\begin{aligned}U_{\alpha\beta}^{(s)}(\phi_x\phi_y;l_3l_3')=\delta_{\alpha\beta}U^{(s)}(\phi_x\phi_y;\,l_3l_3')\;,\\ U^{(s)}(\phi_x\phi_y;\,l_3l_3')=U^{(0)}(\phi_x\phi_y;\,l_3-l_3')\\ +U^{(0)}(\phi_x\phi_y;\,l_3+l_3'-1)\;.\end{aligned} \tag{13}$$

In Eq. (13), $\underline{\underline{\mathrm{U}}}^{(0)}$ is the Green's function of the bulk crystal. A closed analytic expression for $\underline{\underline{\mathrm{U}}}^{(0)}$ may be obtained for the model[13]

$$U^{(0)}(\phi_x\phi_y;\,l_3;\,\omega^2)=(1/\beta)t^{1+|l_3|}/(t^2-1)\;, \tag{14}$$

where, for $\omega^2=0$, only needed here [see Eq. (10)]

$$t=X-(X^2-1)^{1/2}\;, \tag{15}$$

where

$$X=3-\cos\phi_x-\cos\phi_y\;. \tag{16}$$

To calculate the MSD of the atoms in the physisorbed layer, we need to know [Eq. (10)], the Green's function U which may be obtained from the relations

$$U(l_3 l_3') = U^s(l_3 l_3') + \sum_{l_3'' l_3'''} U^s(l_3 l_3'')\delta L(l_3'' l_3''')\, U(l_3''' l_3') \,. \tag{17}$$

Using Eqs. (10) and (13)–(15) and introducing

$$\mu = (\beta' - \beta)/\beta \,, \tag{18a}$$

$$\mu'' = (\beta'' - \beta)/\beta \,, \tag{18b}$$

and

$$\nu = 2\mu''(2 - \cos\phi_x - \cos\phi_y) \,, \tag{19}$$

Eq. (17) reads

$$U(l_3 l_3') = U^s(l_3 l_3') + \beta[(\mu+\nu)U^s(l_3 1) - \mu U^s(l_3 2)]U(1 l_3') + \beta\mu[-U^s(l_3 1) + U^s(l_3 2)]U(2 l_3') \,, \tag{20}$$

where

$$U^s(l_3 l_3') = \frac{1}{\beta}\,\frac{t}{t^2-1}\left(t^{|l_3 - l_3'|} + t^{|l_3 + l_3' - 1|}\right) . \tag{21}$$

From Eq. (20) one obtains a system of two equations for two unknowns $U(1l_3')$ and $U(2l_3')$ which are found to be for $l_3' > 1$

$$U(1 l_3') = [(1+\mu)/\beta]t^{l_3'}/\Delta \,, \tag{22}$$

$$U(2 l_3') = (1/\beta)(t^{l_3'-1}/\Delta)[t^2 + (\mu+\nu-1)t + 1] \,, \tag{23}$$

where

$$\Delta = (1 + 2\mu t - \mu t^2)(t-1) - \nu t(1+\mu t) \,. \tag{24}$$

From Eq. (20), one also easily obtains

$$U(11) = (t/\beta)(1+\mu t)/\Delta \,, \tag{25}$$

and for $n > 1$,

$$U(l_3 l_3) = (t/\beta)(t^{2l_3 - 1} + 1)/(t^2 - 1) + (t^{2(l_3-1)}/\beta\Delta)[\mu(t^3 - 3t^2 + \nu t^2 + 3t - 1) + \nu(1+\mu)t^2/(t-1)] \,. \tag{26}$$

In Sec. IV, we use these results to evaluate the surface MSD and their damping when going away from the surface.

IV. MEAN-SQUARE DISPLACEMENTS OF ATOMS IN A PHYSISORBED MONOLAYER

The high-temperatures mean-square displacements for an atom in the l_3 plane can be obtained from Eq. (10),

$$\langle u^2(l_3)\rangle \simeq -\frac{k_B T}{(2\pi)^2}\int_{-\pi}^{+\pi} d\phi_x \int_{-\pi}^{+\pi} d\phi_y\, U(l_3 l_3) \,. \tag{27}$$

In the Montroll-Potts model, the three branches of vibrations are uncoupled. That is why the Green's functions are independent of the directions $\alpha = x, y, z$. From Eq. (27) we then obtain the same MSD for the three directions of space and in particular the MSD perpendicular and parallel to the surface have the same value. This is not in general the case[1,2] and is due to the model used here. However, the qualitative properties we derive here will remain in a more sophisticated model.[8]

Using the values given by Eqs. (25), (26), (15), and (16) we can calculate from Eq. (27), the MSD for all atoms in the solid with the physisorbed monolayer. This can be done easily by numerical integration. We will however prefer to use simple approximations to obtain the results of interest in closed analytic forms. As we stated at the beginning we are mainly interested here in the contribution of long-wavelength phonons. We will then use a Debye-like approximation and replace the exact value of t given by Eq. (15) by

$$t = 1 - \phi + \tfrac{1}{2}\phi^2 + \cdots \,. \tag{28}$$

In Fig. 2, we plotted the exact values of t for two directions in the two-dimensional Brillouin zone and the value given by Eq. (28). From this comparison we see that our approximation will describe correctly the long-wavelength phonons for

$$0 < \phi < \phi_L \,, \tag{29}$$

where $\phi_L < 1$.

The short-wavelength phonons will be described by the Einstein approximation[10] in the rest of the two-dimensional Brillouin zone. Finally, we will use the approximate expression

$$\langle u^2(l_3)\rangle \simeq -\frac{k_B T}{2\pi}\int_0^{\phi_L} \phi\, d\phi\, U(l_3, l_3; \phi) + \left(1 - \frac{\phi_L^2}{4\pi}\right)\langle u^2(l_3)\rangle_E \,. \tag{30}$$

A. Free surface

To check these approximations, we will first use them to derive the bulk- and free-surface MSD, whose exact values can be obtained from Eqs. (10) and (13):

$$\langle u^2(l_3)\rangle = -k_B T[U^{(0)}(0,0,0) + U^{(0)}(0,0,2l_3 - 1)]_{\omega^2=0} \,. \tag{31}$$

The bulk Green's functions $U^{(0)}(l_1, l_2, l_3)$ are tabulated[14] and one easily obtains

$$\langle u^2(1)\rangle \simeq 0.338 k_B T/\beta \,, \tag{32a}$$

$$\langle u^2\rangle_{\text{bulk}} \simeq 0.252 k_B T/\beta \,. \tag{32b}$$

An expansion in function of l_3 for the perfect-crystal Green's function was obtained[14] when retaining in $\omega^2(\vec{k})$, the terms in k_α^2 and k_α^4 which give,

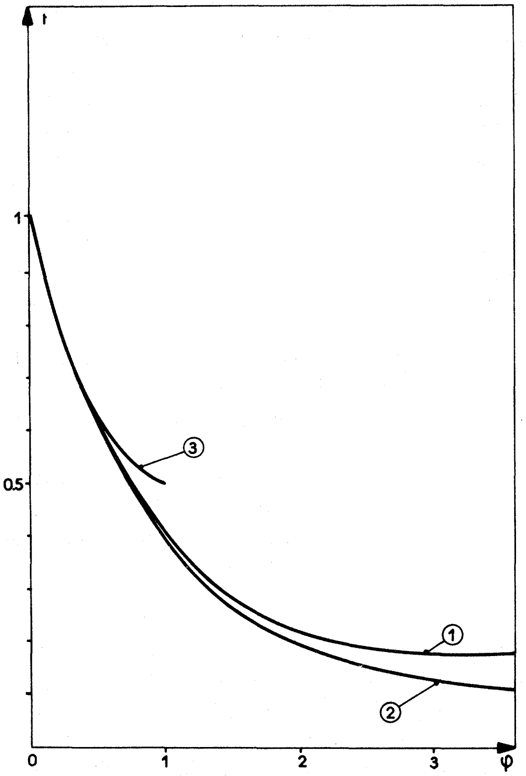

FIG. 2. Exact values of t [Eqs. (15) and (16)] as a function of $\phi = (\phi_x^2 + \phi_y^2)$ for $\phi_y = 0$ (curve 1) and for $\phi_x = \phi_y$ (curve 2). The approximate value of t [Eq. (28)] is given by curve 3.

respectively, the coefficients in l_3^{-1} and l_3^{-3} in the following equation:

$$[U^0(0, 0, l_3)]_{\omega^2=0} = -\frac{1}{4\pi\beta l_3}\left(1 + \frac{1}{4l_3^2} + \cdots\right). \quad (33)$$

The decay in function of l_3 displayed in expansion (33) is due to the low-frequency acoustic phonons. The high-frequency acoustic and (*a fortiori* the optical phonons of a more sophisticated model) do not contribute to this result.

From the above remarks, one sees that the dependence on l_3 exhibited in expansion (33) is completely general. When going to a more sophisticated model, one will have only another dependence on the force constants β in front of the l_3^{-1} and l_3^{-3}. Already for $l_3 = 3$, expansion (33) is approaching the exact result[14] with a precision of 4% with the first term in $(1/l_3)$ and with a precision of 1% with the two terms displayed in Eq. (33). Then we obtain

$$\frac{\langle u^2(l_3)\rangle - \langle u^2\rangle_B}{\langle u^2\rangle_B} \simeq \frac{0.989}{\pi(2l_3 - 1)}\left(1 + \frac{1}{4(2l_3-1)^2} + \cdots\right) \quad (34)$$

Relation (34) already holds for the first layer under the surface with a precision of 4% with the first term and with a precision of 1% with the two terms given above.

From the above discussion, one sees that for $l_3 \gg 1$ the term in Eq. (34), inversely proportional to the depth, is derived in the elastic approximation and that when going to a more sophisticated model, one will just have the multiplicative factor appearing in front of this l_3^{-1} term function of c_l and c_t rather than of the mean value $c = a_0(\beta/M)^{1/2}$ used in this model.

The preceding theoretical investigations reviewed in Refs. 1 and 2 do not give the surface MSD outside the immediate neighborhood of the surface. We feel that it is as important to know how the surface MSD decay away from the surface as their value in the immediate neighborhood of the surface. Müsser[15] gave numerical results for the MSD in a 48-layer crystal. His numerical approach did not allow him to predict that the surface-induced enhancement of the high-temperature MSD of an atom in layer l_3 was inversely proportional to l_3, at large l_3. Equation (30) applied to the case of a free surface (with $\phi_L = 1$) gives, for the long- and short-wavelength contributions,

$$\langle u^2(1)\rangle \simeq (k_BT/\beta)(0.116 + 0.184) = 0.300 k_BT/\beta\,, \quad (35a)$$

$$\langle u^2\rangle_B \simeq (k_BT/\beta)(0.079 + 0.153) = 0.232 k_BT/\beta\,. \quad (35b)$$

We could improve approximation (30) by taking into account the first correction[10] to the Einstein approximation which better describes the short-wavelength phonons by including into the Einstein approximation the first-nearest-neighbors contribution. We do not do it since we are primarily interested here in the long-wavelength contribution. It is also easy to derive in this approach Eq. (34) when noting that far from the surface ($l_3 \gg 1$) the short-wavelength contribution to the MSD of two neighbors planes will be the same, then the variation will be due to long-wavelength contribution. Using Eqs. (14), (31), and (28) one again finds the result given by Eq. (34).

B. Physisorbed monolayer

The MSD calculation for an atom in the physisorbed layer is done along the same lines as above. Putting expressions (24), (25), and (28) into Eq. (30), we obtain

$$\langle\langle u^2(1)\rangle\rangle = \frac{k_B T}{2\pi\beta}\int_0^{\phi_L} d\phi\,\frac{1+\mu-(1+2\mu)\phi+(1+4\mu)\frac{1}{2}\phi^2}{1+\mu+(1+\mu)(\mu''-\frac{1}{2})\phi-\mu(1+\mu'')\phi^2} + \left(1-\frac{\phi_L^2}{4\pi}\right)\frac{k_B T}{4\beta''+\beta'}\;. \tag{36}$$

The denominator of the integrand in Eq. (36) can never be zero, as its exact value Δ [Eq. (24)] has no zeros. From a physical point of view this means that in the model studied here there is no soft surface phonons and that the approximation (28) should not introduce them. Soft-surface phonons could of course exist in a more realistic model especially if one took into account the first derivatives of the interatomic potentials.[11]

The above condition is satisfied in the case which motivated this calculation ($\beta' \ll \beta'' \lesssim \beta$). In this limit, Eq. (36) takes after integration the simplest form for $\phi_L = 1$:

$$\langle\langle u^2(1)\rangle\rangle \simeq \frac{k_B T}{4\pi\beta''}\left[\ln\left(\frac{\beta''}{\beta'}\right) - 3 + 6\left(\frac{\beta'}{\beta''}\right)^{1/2}\tan^{-1}\frac{4\beta}{\beta+2\beta''}\left(\frac{\beta''}{\beta'}\right)^{1/2}\right] + \left(1-\frac{1}{4\pi}\right)\frac{k_B T}{4\beta''}\;. \tag{37}$$

This expression shows that for $\beta''/\beta' > 100$, the $\ln(\beta''/\beta')$ term is the leading one for the MSD of an atom in the physisorbed layer.

It is interesting also to see from Eqs. (26) and (30) that here as well as in the case of a free surface discussed above, the difference $\langle\langle u^2(l_3)\rangle\rangle - \langle u^2\rangle_B$ is proportional to $1/l_3$ for $l_3 \gg 1$. In Sec. V, we turn to a physical discussion of the results given in this section.

V. CONCLUSION

The results of this paper, we want to stress, are more of a qualitative than quantitative nature. First, the difference between surface (with or without an adsorbed layer) and bulk MSD is proportional to the inverse of the depth l_3 for $l_3 \gg 1$. Second, when a two-dimensional solid is physisorbed on a crystal surface, the substrate tends to stabilize it even for a weak coupling β' between adsorbate and substrate as the divergence in the MSD for β' going to zero is of a logarithmic type.

In a more sophisticated model, the MSD parallel and perpendicular to the surface would no longer be equal. This paper shows that the "frozen-substrate" approximation leads to the same logarithmic divergence when $\beta' \ll \beta''$, as an exact analysis. We can then study the same problem for a realistic model using the same "frozen-substrate" approximation. It is straightforward to see that in general one can define different parameters for vibrations parallel and perpendicular to the surface, respectively, ($\beta'_{\parallel}, \beta''_{\parallel}$) and $\beta'_{\perp}, \beta''_{\perp}$). For $\beta'_{\perp} \ll \beta''_{\perp}$ and $\beta'_{\parallel} \ll \beta''_{\parallel}$, one will obtain in the same way as in this paper,

$$\langle\langle u^2(1)\rangle\rangle_{\parallel} \propto \ln\beta''_{\parallel}/\beta'_{\parallel}\;, \quad \langle\langle u^2(1)\rangle\rangle_{\perp} \propto \ln\beta''_{\perp}/\beta'_{\perp}\;.$$

The interesting physical point is to know if $\langle\langle u^2(1)\rangle\rangle_{\parallel}$ can be bigger or smaller than the $\langle\langle u^2(1)\rangle\rangle_{\perp}$ when this logarithmic term is the leading one, as these two situations have clearly different physical meanings. In the first case one could expect the physisorbed layer to slide on the surface after losing long-range order. In the second case desorption would be the leading effect.

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